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## Producing milli-Kelvin samples of ammonia molecules

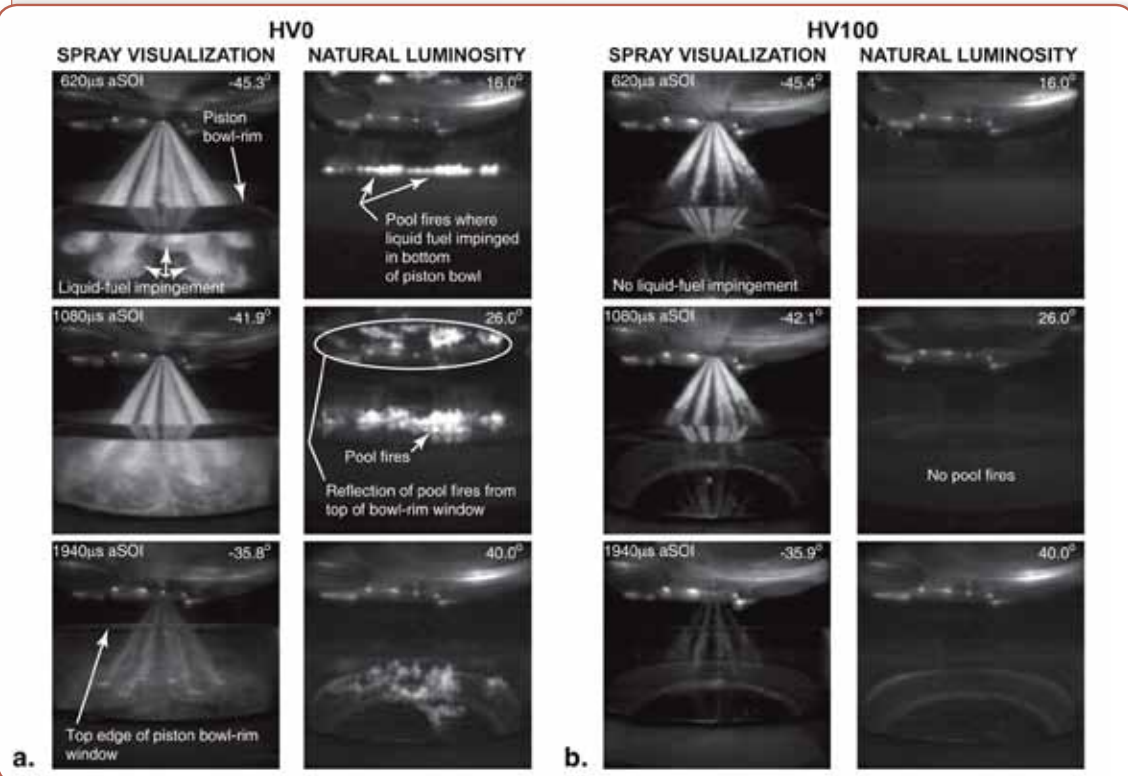
Molecules at sub-Kelvin temperatures have recently attracted the interest of chemists and physicists in part because their low velocities mean that they can be observed for a long period of time. This long observation time removes the main sources of line broadening in spectroscopic measurements, and spectra of cold molecules may be acquired with such high resolution and precision that they can be used to test fundamental physical models. For example, ultrahigh-resolution spectra of cold OH and ND<sub>3</sub> are expected to reveal information about time variation in fundamental physical constants, and spectra of heavier molecules such as YbF may confirm or deny the existence of an electron electric dipole moment. Measurements this precise require samples of molecules with temperatures on the order of a few milli-Kelvin (1/1000 of a degree Kelvin). There are very few techniques for cooling molecules to these temperatures.

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## Increasing diesel fuel volatility can significantly improve efficiency and emissions under early direct-injection, low-temperature combustion conditions

Improving efficiency while complying with current and future emissions legislation is a serious challenge for engine designers. Researchers Charles Mueller and Brian Fisher of Sandia, Glen Martin of Caterpillar

Technical Center, and Professor A.S. (Ed) Cheng of San Francisco State University have been exploring the potential of low-temperature combustion (LTC) to meet these goals. One way to achieve LTC in a



**Figure 1.** Images from spray-visualization and natural-luminosity movies acquired for: (a) a conventional ultra-low-sulfur #2 diesel fuel (HVO), and (b) a higher-volatility mixture of 20 vol% toluene with balance *n* heptane (HV100). All images were acquired by viewing through a window in the cylinder wall. The spray-visualization images in (a) show that the lower-volatility HVO leads to impingement of liquid fuel on the top of the piston, and the natural-luminosity images show that pool fires are observed later in the cycle at the impingement locations. In contrast, the images in (b) show that the higher-volatility HV100 does not exhibit liquid-fuel impingement or pool fires. The crank angle after top dead center (ATDC) at which each image was acquired is shown in the upper-right corner of each image frame. The engine operating parameters for all images are: 1200 rpm speed, 4.82 bar gross indicated mean effective pressure load, actual start of injection  $-50^{\circ}$  ATDC,  $42^{\circ}\text{C}$  intake temperature, 1.42 bar intake manifold pressure (abs.), 50% exhaust gas recirculation (simulated), 142 MPa injection pressure, and a dual-row injector tip with 15 orifices of  $103\text{ }\mu\text{m}$  diameter (5 orifices at  $35^{\circ}$  included angle and 10 orifices at  $70^{\circ}$  included angle).

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## Increasing diesel fuel volatility (continued)

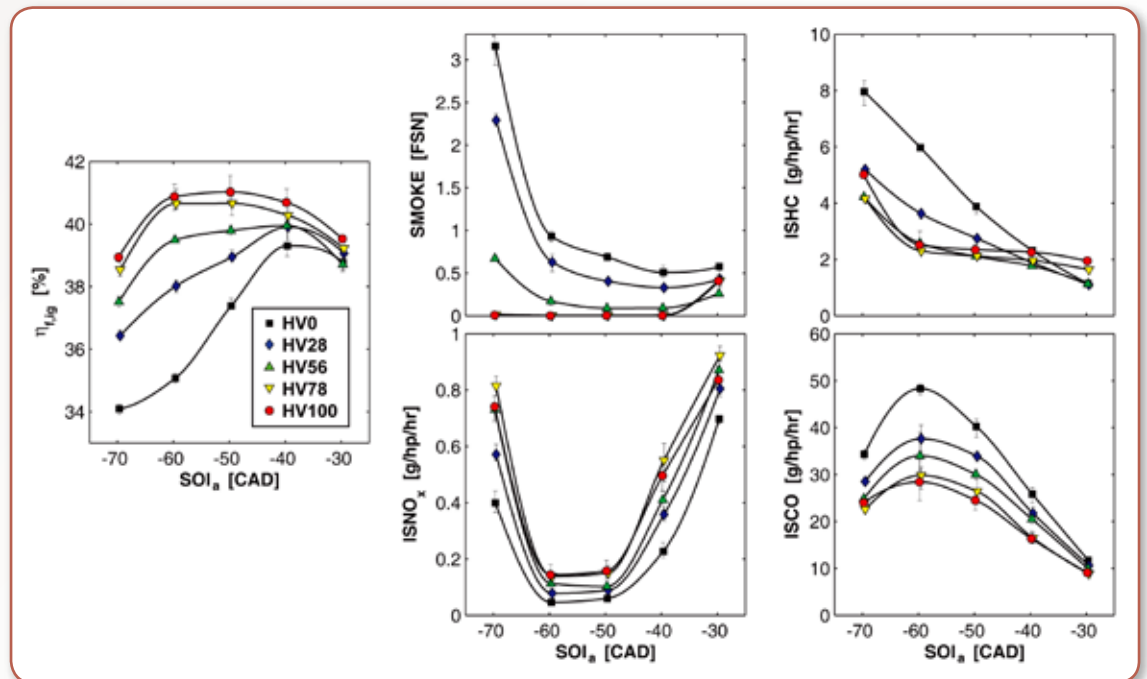
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diesel engine is to inject the fuel early (well before top-dead-center) in the compression stroke so that it has more time before ignition to vaporize and premix to sufficiently fuel-lean conditions that emissions of nitrogen oxides ( $\text{NO}_x$ ) and smoke are minimized. Collaborative DOE- and Caterpillar-sponsored work in the Advanced Fuels Laboratory within Sandia's CRF has shown that a principal barrier to success with this type of approach is the creation of liquid fuel films on in-cylinder surfaces. These films form because fuel that is injected into the cool-

er, less-dense charge in the cylinder early in the compression stroke is more difficult to vaporize, and it can penetrate far enough through the combustion chamber that impingement can occur on the piston or cylinder wall. Since increasing fuel volatility should enhance vaporization and mitigate wall impingement, a study of fuel-volatility effects on efficiency and emissions was conducted using an early direct-injection LTC strategy. An injector nozzle with a narrow included angle and small orifices was used in the experiments to further decrease the potential for wall impingement.

The understanding of the relationships among fuel films, efficiency, and emissions obtained from the experiments can be summarized as follows. Liquid fuel films on in-cylinder surfaces should be avoided. For the conditions studied (which are representative of those proposed for future engine operating modes), the formation of fuel films can occur, leading to incomplete combustion, which in turn can cause increased fuel consumption and dilution of the lubricating oil. In addition, if the fuel vapor above a

film ignites to produce an intensely luminous pool fire, the fuel-rich combustion produces soot well into the expansion stroke when bulk-gas temperatures and mixing rates are insufficient to oxidize it, leading to elevated smoke emissions. Meanwhile, near-stoichiometric regions around the rich mixture can produce  $\text{NO}_x$  emissions. Radiative heat transfer from the pool fire to the fuel film enhances vaporization and combustion of the film, yielding lower unburned hydrocarbon (HC) and carbon monoxide (CO) emissions



**Figure 2.** Gross indicated fuel-conversion efficiency ( $\eta_{i,g}$ ), smoke, and indicated-specific nitrogen oxides (ISNO<sub>x</sub>), unburned hydrocarbons (ISHC), and carbon monoxide (ISCO) emissions for HV0, HV28, HV56, HV78, and HV100 over a range of actual start-of-injection (SOI<sub>i</sub>) timings. All other operating conditions are the same as those listed in the caption of Figure 1. In general, efficiency increases and smoke, HC, and CO emissions decrease as fuel volatility is increased, while  $\text{NO}_x$  emissions for intermediate SOI<sub>i</sub> timings at this steady-state operating condition remain below the 0.2 g/hp/hr limit for 2010 on-highway truck engines.

than if an intensely luminous pool fire is not produced; nevertheless, HC and CO emissions are still high enough to require the use of an oxidation catalyst to meet emissions regulations. On the other hand, if an intensely luminous pool fire is not produced above a fuel film, hot soot is not formed in the vapor region above the film. The lack of heat transfer to the film from radiating soot in a pool fire inhibits film vaporization and subsequent combustion, leading to even higher HC and CO emissions.  $\text{NO}_x$  emissions may be high or low in this latter case, since they are controlled primarily by the bulk-gas mixture (particularly in the absence of a pool fire).

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## Bert Debuschere honored with a Presidential Early Career Award for Scientists and Engineers

In a ceremony conducted at the White House on December 19, 2008, with President George Bush attending, Bert Debuschere of Sandia's CRF and 66 other researchers received the nation's highest honor for professionals at the outset of their scientific careers, the 2007 Presidential Early Career Award for Scientists and Engineers. Dr. John H. Marburger III, Science Advisor to the President and Director of the White House Office of Science and Technology Policy, presided over the ceremony.

Eight recipients were given awards from the Department of Energy, as shown above holding their plaques, from left to right: Jennifer S. Martinez, Los Alamos National Laboratory, Yugang Sun, Argonne National Laboratory, Wei Pan, Sandia National Laboratories, Jeanine Cook, New Mexico University (seated), Mickey G. Chiu, Brookhaven National Laboratory, Hooman Davoudiasl, Brookhaven, Robin Santra, Argonne National Laboratory, and Bert Debuschere, also shown at right. In the center standing are DOE Under Secretary for Science Dr. Raymond L. Orbach and NNSA Deputy Administrator for Defense Programs Robert Smolen..



## Dick Steeper honored by Society of Automotive Engineers

Dick Steeper has been honored by the Society for Automotive Engineers (SAE) with a 2009 Forest McFarland Award. Only about 20 Forest McFarland Awards are given each year; Dick is the fifth Sandian to receive the award. The Forest McFarland Award recognizes individuals for their outstanding contributions toward the work of the SAE Engineering Meetings Board (EMB) in the planning, development, and dissemination of technical information through technical meetings, conferences, and professional development programs or outstanding contributions to the EMB operations in facilitating or enhancing the interchanges of technical information. Dennis Siebers, Dick's manager, commented that "Sandia's engagement in technical societies is an important aspect of our service to the nation. It's great to see that Dick's hard work for the SAE over several years is being recognized."

Dick and Paul Miles, a 2002 McFarland Award recipient, are currently the co-vice chairs of the SAE Powertrain, Fuels, and Lubes (PF&L) Activity—a large division of SAE's Land and Sea Group. This activity plays a central role in organizing the technical program of three major international meetings each year—the World Congress, the Fall PF&L meeting, and the Spring international meeting—as well as other SAE events. The role of the vice-chair is to assist the chair in organizing SAE meetings. "Our goal is to make the meetings as meaningful as possible," Dick says. "SAE meetings are extremely valuable as a place to disseminate timely results to the transportation research community." SAE is the prime location for publishing such research. The faster turnaround than other journals—6 months compared with a year or more for other venues—aids in the dissemination of new work.

Dick is also a member of SAE's Technical Quality Response Team tasked with implementing quality standards for SAE publications. A current focus is to include SAE journal papers in the Science Citation Index. Dick and Paul will assume the Chair of the SAE Powertrain, Fuels, and Lubes activity at the end of their 3-year term as vice-chairs.

## Foreign visitor to CRF over the holidays



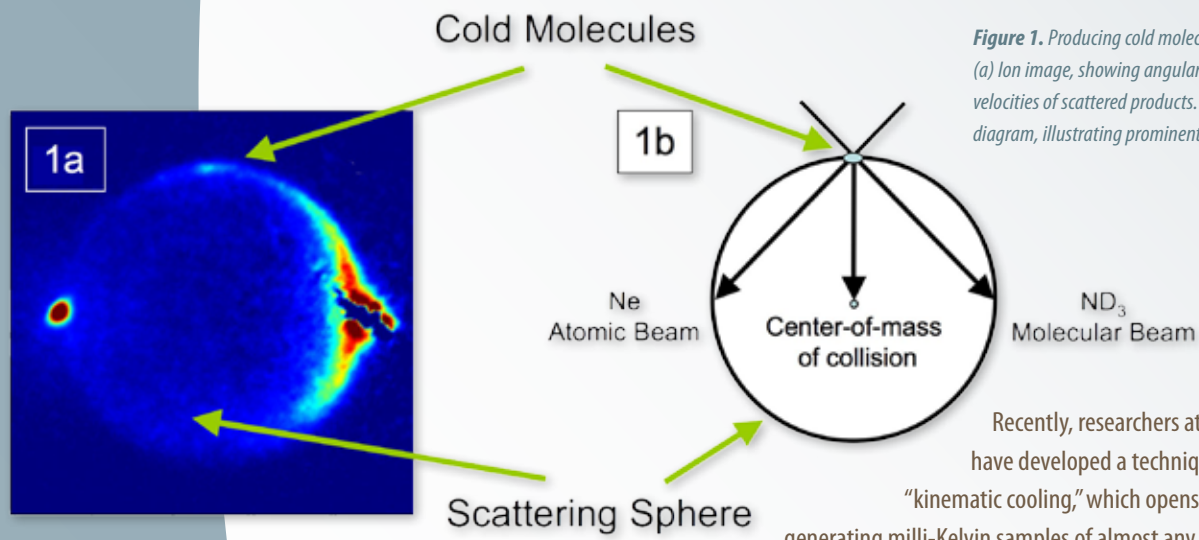
**Mr. Renard Roux recently visited the CRF over the holiday break. He has not yet declared his particular area of research and technology, but we are pretty certain it will be green.**



Photos by Charles Mueller

# Producing milli-Kelvin samples of ammonia molecules

(Continued from page 1)



**Figure 1.** Producing cold molecules by scattering. (a) Ion image, showing angular distribution and velocities of scattered products. (b) Scattering diagram, illustrating prominent features in (a).

Recently, researchers at Sandia have developed a technique known as “kinematic cooling,” which opens the door to generating milli-Kelvin samples of almost any small molecule, potentially opening the field to a wider scientific audience. In kinematic cooling, molecules collide with atoms of similar mass in a crossed beam apparatus, and after some of these collisions, the molecules are left nearly stationary in the laboratory frame. These molecules have velocities of a few m/s, and therefore a temperature of a few milli-Kelvin. By changing the masses and velocities of the collision partners, it is also possible to create cold samples in any quantum state that can be populated by collisions.

To demonstrate the viability of kinematic cooling as a forefront technique, CRF researchers Jeffrey Kay, Kevin Strecker, and David Chandler, in collaboration with Sebastiaan van de Meerakker of the Max Planck Society in Berlin, have embarked on a campaign to cool and electrostatically trap ND<sub>3</sub> molecules. The goal is to demonstrate that kinematic cooling produces quantities of cold molecules large enough to be useful in routine experiments. The first step has been successfully achieved; samples of milli-Kelvin ND<sub>3</sub> molecules have been prepared and detected in the laboratory.

$(J, K)$	$v'_{\text{ND}_3}$ (meas.)	$\bar{E}_{\text{trans}} / k$ (meas.)	$v'_{\text{ND}_3}$ (calc.)	$\bar{E}_{\text{trans}} / k$ (calc.)
(2, 0)	26 ± 20 m/s	810 mK	16 ± 0.6 m/s	310 mK
(2, 1)	27 ± 18 m/s	880 mK	11 ± 0.4 m/s	140 mK
(2, 2)	23 ± 16 m/s	640 mK	8 ± 0.3 m/s	70 mK
(3, 1)	28 ± 16 m/s	940 mK	27 ± 1.0 m/s	880 mK
(3, 2)	21 ± 17 m/s	530 mK	24 ± 0.8 m/s	680 mK
(3, 3)	32 ± 26 m/s	1.2 K	23 ± 0.8 m/s	630 mK

**Table 1.** Measured and calculated velocities and temperatures of cold ND<sub>3</sub> molecules. Temperature is defined as the ratio of the average kinetic energy to the Boltzmann constant  $k$ .

In the kinematic cooling step, ND<sub>3</sub> molecules are brought to rest by velocity-cancelling collisions with neon atoms. A molecular beam of ND<sub>3</sub> intersects an atomic beam of neon at 90 degrees, and some of the ND<sub>3</sub> molecules are scattered at just the right angle so that their center-of-mass velocity exactly cancels the velocity of the center of mass of the collision pair. A schematic of the experimental arrangement is shown in Figure 1b. When this occurs, the molecules are left stationary in the laboratory frame, and are therefore translationally “cold.” The recoiling molecules are then resonantly ionized and projected onto an imaging detector, resulting in a “velocity-mapped” image that directly displays the velocity distribution of scattered products. A typical velocity-

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## Producing milli-Kelvin samples of ammonia molecules (continued)

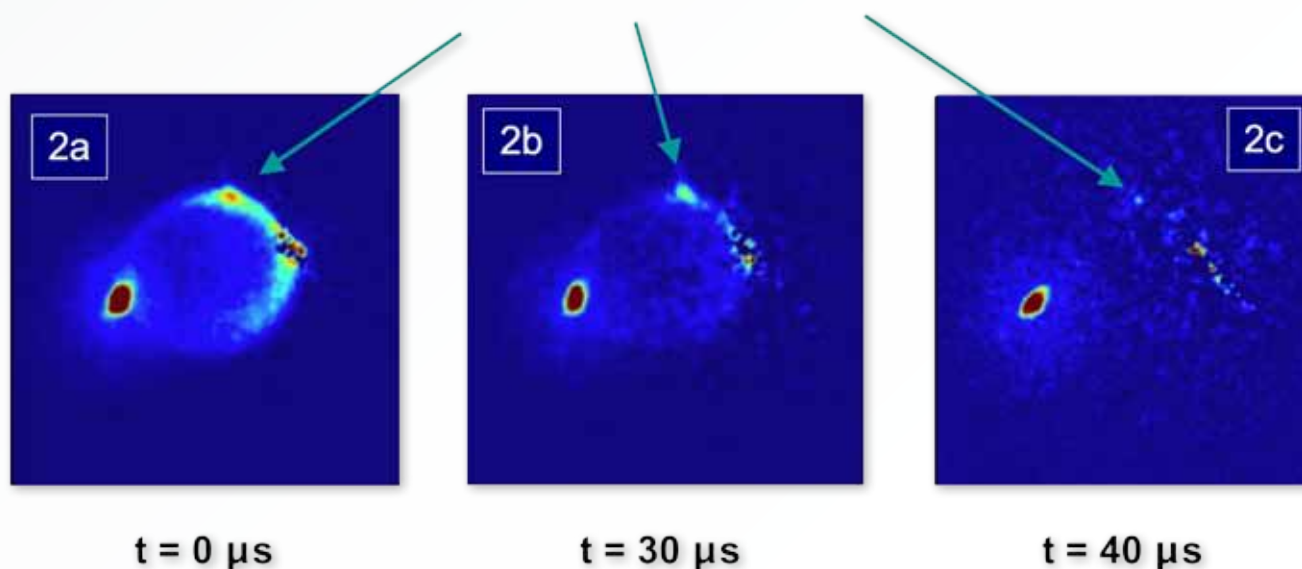
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mapped ion image is shown in Figure 1a. As seen in the figure, a maximum appears near the top of the image, corresponding to  $\theta = 90^\circ$  scattering, and is caused by an accumulation of molecules moving slowly in the laboratory frame. These are the molecules that have been cooled by velocity-cancelling collisions.

The collisions populate many different rotational states, which are labeled by the quantum numbers  $J$  (the total angular momentum) and  $K$  (the projection of  $J$  along the  $C_3$  axis of the molecule). Ammonia in the  $(J, K) = (2,0), (2,1), (2,2), (3,1), (3,2)$  and  $(3,3)$  quantum states have been successfully cooled, and velocities and effective temperatures are shown in Table 1. Although in most cases the measured temperatures are less than 1 K, by its nature the measurement overestimates the final velocities, and in all cases calculation indicates that the molecules are actually much colder.

The fact that the cold ammonia molecules are spatially located at the crossing point of the atomic and molecular beams poses a serious challenge for the trapping phase of the experiment. Secondary collisions with these hot atoms and molecules reheat the cold ammonia and knock it out of the collision volume. Recent experimental advances have allowed the researchers to both extract the ammonia molecules from the hot environment and prevent unwanted portions of the parent beams from entering the collision volume. This condition is shown in Figure 2. Experimental conditions have been found such that the beams and the bulk of the scattering are gone but the cold ammonia molecules, seen as a spot on the detector, remain. These cold molecules are available to be trapped and held for long periods of time. At the time of this writing, the cooling step of the experiments is complete, and the researchers are now attempting to trap cold  $\text{ND}_3$ . Results pertaining to the first step have been accepted for publication in *Faraday Discussions*.

### Cold Molecules, during and after collisions between atomic and molecular beams



**Figure 2.** Cold molecules persist while fast-moving molecules fly away. (a) Ion image near scattering peak. Fast-moving and slow-moving scattered products are detected. (b) Image acquired 30 microseconds later. Scattering is faint and only slow molecules are detected efficiently. (c) Image acquired 40 microseconds later. Only slow molecules created at much earlier times are detected.



Increasing diesel fuel volatility (continued)

(Continued from page 2)

The observations above are the result of optical-engine experiments using a conventional ultra-low-sulfur #2 diesel fuel (HV0), a high-volatility mixture of 20 vol% toluene with balance *n*-heptane (HV100), and blends of 28, 56, and 78 vol% of HV100 in HV0 (denoted HV28, HV56, and HV78, respectively). It is noted that HV100 was formulated to have approximately the same ignition quality as HV0 so that the results represent, as much as possible, the effect of changing fuel volatility only (given the compositional differences between HV0 and HV100). Figure 1 shows selected frames from spray-visualization and natural-luminosity movies acquired with HV0 and HV100; and Figure 2 shows the efficiency and emissions

data for all of the fuels. The figures show that the absence of liquid-fuel impingement on in-cylinder surfaces is accompanied by substantial improvements in efficiency, smoke, HC, and CO, while NO<sub>x</sub> compliance with 2010 on-highway engine regulations (0.2 g/hp/hr) is maintained for intermediate injection timings. The simple conceptual understanding gained through these experiments, as outlined above, is consistent with and helps unify fuel-effects trends reported in the literature. Such an enhanced understanding can assist engine designers and fuel producers in identifying improved operating strategies and fuel specifications for the future.

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